

1 Glass like material with improved safety characteristics.

2

3 The present invention relates to a glass-like material
4 which has improved safety characteristics compared to
5 ordinary glass.

6

7 In the present Application references to a "glass-like"
8 material refer to a material having the following
9 characteristics; clarity, brittleness, low strain to
10 failure and rigidity.

11

12 Ordinary glass is used in a variety of everyday
13 applications. For example it is known in the art to use
14 glass as a protective covering over fire and other types
15 of emergency alarms, emergency door releases, emergency
16 stop buttons on public transport, fire extinguishers,
17 fire axes and the like. As glass is transparent persons
18 can quickly and easily identify the presence of the alarm
19 or apparatus in the retaining box. If required, the
20 glass can be broken in order to access the alarm or
21 device.

22

23 However an inherent problem lies in the manner in which
24 the glass can be broken. Often a subsidiary device such

1 as a hammer is supplied with, or near to, the alarm or
2 apparatus, and can be used to break the glass. However,
3 in the event that this device is missing or cannot be
4 located in an emergency situation it will be necessary
5 for the person who wishes to access the apparatus or
6 alarm to break the glass by some other means. In the
7 event of an emergency situation the person may use, for
8 example, a hand or elbow for this purpose, and may, as a
9 result, sustain injuries from breaking the glass.

10 Breakage of glass results in the production of sharp
11 glass fragments and splinters, which can cause injury to
12 the user or other persons in the proximity of the alarm
13 or apparatus. In addition the potential risk of injury
14 from breaking the glass may cause hesitation on the part
15 of the person who wishes to access the alarm or
16 apparatus, having dangerous consequences.

17

18 The glass may also be broken by malicious or accidental
19 damage. Whilst the glass fragments can be removed and
20 the retaining glass replaced, there is an interim risk of
21 injury to persons coming into contact with the broken
22 fragments.

23

24 Considerable research has been conducted to find
25 materials which can be used in Applications similar to
26 glass but which minimise the risk of damage to persons in
27 the instance of the material being broken either
28 intentionally or accidentally. Safety glass i.e.
29 toughened glass, materials are well known in the art and
30 have numerous applications and uses. Most have enhanced
31 safety by virtue of being reinforced in strength, such
32 that they have a higher stress to failure than glass; in
33 other words a greater force is needed to shatter or break
34 them than would be required with ordinary glass. Uses

1 vary from windows and doors on automobiles and public
2 transport, to domestic uses such as shower enclosures and
3 room partitions. Whilst in many instances these have
4 greatly increased safety, they are of limited use in
5 Applications where it is actually desirable for the glass
6 to be broken, i.e. when used on retaining boxes of
7 emergency apparatus and alarms, because of their enhanced
8 strength and resistance to force.

9

10 For example the polymeric materials Perspex™ and
11 Plexiglas™, are transparent like glass, and do not pose
12 the same risk of injury when broken. However, these
13 materials can be harder to break than glass and can still
14 produce sharp fragments when broken.

15

16 In addition, the containers in which alcoholic drinks,
17 carbonated soft drinks and oxygen sensitive juices are
18 sold are also traditionally manufactured from glass.
19 Glass bottles are well received by consumers as they
20 impart the impression of a high quality product and have
21 "chink factor". Nevertheless, the use of bottles is
22 inherently dangerous, as glass is easily broken. It will
23 be appreciated that this is a particular problem in bars,
24 pubs and nightclubs, where accidental breakage of glass
25 bottles, is a potential health risk.

26

27 Glass bottles are also disliked as they can be used
28 deliberately, as weapons, to inflict damage on other
29 persons. In fact, safety regulators have actively
30 encouraged drinks manufacturers, as well as
31 establishments which serve drinks and alcohol, to use
32 bottles and glasses made from non-dangerous materials, in
33 order to reduce the number of serious injuries caused by
34 glass and bottle attacks.

1
2 In recent years there has been a move towards providing
3 bottles manufactured from materials which are not as
4 dangerous as glass. It is estimated that packaged beer
5 production world wide in 1996 was 106.6 billion litres,
6 requiring 186.2 billion bottles and 73.7 billion cans.
7 The beer bottle market was forecasted to grow at an
8 annual rate of three percent through 2001 to 216 billion
9 units. Most bottle production makes use of glass with
10 only 0.1 billion plastic bottles being utilised in 1996.
11 However due to the push towards increased safety it is
12 estimated that the demand for plastic bottles is forecast
13 to reach 2.5 billion by 2006.

14
15 The focus on safer bottles is particularly important with
16 respect to alcoholic drinks, which are consumed in bars
17 and nightclubs. PET, poly(ethylene terephthalate), a
18 plastic which can be readily manufactured into bottles,
19 and which does not break as readily as glass, has already
20 been used for this purpose.

21
22 However the use of PET poses its own problems to the
23 industry. PET is a relatively expensive material and not
24 cheap to process which makes it a less popular option for
25 drinks manufacturers. In addition, there is a general
26 consensus that plastic bottles are not as well received
27 by the public as they feel cheaper and do not have the
28 same high quality feel as glass.

29
30 It is therefore an object of at least one aspect of the
31 present invention to provide a material which resembles
32 glass, but which has improved safety characteristics when
33 compared to ordinary glass.

34

1 It is also an object of at least one aspect of the
2 present invention to overcome the problems that are
3 described above with reference to existing glass and
4 plastic bottles.

5
6 According to a first aspect of the present invention
7 there is provided a material which shatters, when broken,
8 into fragments which do not cut, puncture or otherwise
9 damage human skin or tissue, wherein the material is
10 comprised of an amorphous thermoplastic polymer and one
11 or more low molecular weight resins.

12
13 Preferably the material is comprised of a simple mixture
14 of amorphous thermoplastic polymer and one or more low
15 molecular weight resins.

16
17 Preferably the amorphous thermoplastic polymer is chosen
18 from the group consisting of polystyrene (PS), polymethyl
19 methacrylate (PMAA), styrene-acrylonitrile copolymer
20 (SAN), linear polyesters and co-polyesters and
21 polycarbonate (PC).

22
23 The one or more low molecular weight resins chosen will
24 be completely compatible with the chosen polymer. For
25 example in the case of polystyrene the low molecular
26 weight resin is typically C9 aromatic hydrocarbon resin.

27
28 Preferably the material has a tensile stress limit of
29 between 11 and 60 Nmm⁻².

30
31 Preferably the low molecular weight resin will have a Mn
32 (number average molecular weight) such that it has less
33 than 500 repeating units, and preferably less than 50
34 repeating units.

1

2 The material may be manufactured in sheet form.

3

4 According to a second aspect of the present invention
5 there is provided a polymeric blend comprising a polymer
6 selected from the group consisting of: polystyrene, (PS),
7 polymethyl methacrylate (PMAA), styrene-acrylonitrile
8 copolymer (SAN), linear polyesters and co-polyesters and
9 polycarbonate (PC) and one or more low molecular weight
10 resins.

11

12 The one or more low molecular weight resins chosen will
13 be completely compatible with the chosen polymer. For
14 example in the case of polystyrene the low molecular
15 weight resin is typically C9 aromatic hydrocarbon resin.

16

17 Preferably the one or more low molecular weight resins
18 have a Mn (number average molecular weight) such that it
19 has less than 500 repeating units, and preferably less
20 than 50 repeating units.

21

22 Preferably the one or more low molecular weight resins
23 are hydrocarbon resins.

24

25 Preferably the one or more low molecular weight resins
26 are aromatic hydrocarbon resins.

27

28 The polymeric blend may be manufactured in sheet form.

29

30 According to a third aspect of the present invention
31 there is provided a material which shatters, when broken,
32 into fragments which do not cut, puncture or damage human
33 skin or tissue, the material being comprised of
34 polystyrene and one or more low molecular weight resins.

1
2 Preferably the material is comprised of a simple mixture
3 of polystyrene and one or more low molecular weight
4 resins.

5
6 Preferably the one or more low molecular weight resins
7 are hydrocarbon resins.

8
9 Preferably the one or more low molecular weight resins
10 are aromatic hydrocarbon resins.

11
12 Most preferably the one or more low molecular weight
13 hydrocarbon resins are C9 aromatic hydrocarbon resins.

14
15 Preferably the one or more low molecular weight resins
16 are, or are derived from, alpha methyl styrene.

17
18 Preferably the one or more low molecular weight
19 hydrocarbon resins are selected from a group consisting
20 of; NorsoleneTM, KristalexTM, PlastolynTM EndexTM,
21 PiccotexTM, PiccolasticTM, SukorezTM or ArkonTM.

22
23 Most preferably the one or more low molecular weight
24 hydrocarbon resins are selected from a group consisting
25 of; Norsolene W90TM, Norsolene W100TM, Norsolene W110TM,
26 Kristalex F85TM, Kristalex F100TM, Kristalex F115TM,
27 Plastolyn 240TM, Plastolyn 290TM, Endex 155TM,
28 Piccolastic D125TM, Sukorez 100TM, Sukorez 120TM, Arkon
29 P100TM, Arkon P125TM, Arkon P140TM, Piccotex 75TM,
30 Piccotex 100TM or Piccotex 120TM.

31
32 Preferably the one or more low molecular weight resins
33 will have a Mn (number average molecular weight) such

1 that it has less than 500 repeating units, and preferably
2 less than 50 repeating units.

3

4 Preferably the material has a tensile stress limit
5 between 11 and 60 Nmm⁻².

6

7 Optionally the material may also include UV inhibitors,
8 antioxidants, flow modifiers, fire retarding agents,
9 colour pigments and brighteners as known in the art.

10

11 The material may be manufactured in sheet form.

12

13 According to a fourth aspect of the present invention
14 there is provided a method of manufacturing a material
15 which shatters, when broken, into fragments which do not
16 cut, puncture or damage human skin or tissue, the method
17 comprising the step of mixing an amorphous thermoplastic
18 polymer and one or more low molecular weight resins.

19

20 Preferably the amorphous thermoplastic polymer is chosen
21 from the group consisting of polystyrene (PS), polymethyl
22 methacrylate (PMAA), styrene-acrylonitrile copolymer
23 (SAN), linear polyesters and co-polyesters and
24 polycarbonate (PC).

25

26 Preferably the one or more low molecular weight resins
27 are completely compatible with the chosen polymer. For
28 example in the case of polystyrene preferably the chosen
29 low molecular weight resin is C9 aromatic hydrocarbon
30 resin.

31

32 Preferably the one or more low molecular weight resins
33 are hydrocarbon resins.

34

1 Preferably the one or more low molecular weight resins
2 are aromatic hydrocarbon resins.

3

4 Preferably the low molecular weight resin will have a Mn
5 (number average molecular weight) such that it has less
6 than 500 repeating units, and preferably less than 50
7 repeating units.

8

9 Preferably as the polystyrene is mixed with the one or
10 more low molecular weight hydrocarbon resins, the glass
11 transition temperature (T_g) of the material is elevated.
12 Typically the T_g is elevated to 5-10 degrees C higher
13 than the base polymer.

14

15 According to a fifth aspect of the present invention
16 there is provided a method of manufacturing a material
17 which shatters, when broken, into fragments which do not
18 cut, puncture or damage human skin or tissue, the method
19 comprising the step of mixing polystyrene and one or more
20 low molecular weight hydrocarbon resins.

21

22 Preferably the one or more low molecular weight resins
23 are hydrocarbon resins.

24

25 Preferably the one or more low molecular weight resins
26 are aromatic hydrocarbon resins.

27

28 Most preferably the one or more low molecular weight
29 hydrocarbon resins are C9 aromatic hydrocarbon resins.

30

31 Preferably the one or more low molecular weight resins
32 are, or are derived from, alpha methyl styrene.

33

1 Preferably the one or more low molecular weight
2 hydrocarbon resins are selected from a group consisting
3 of; NorsoleneTM, KristalexTM, PlastolynTM EndexTM,
4 PiccotexTM, PiccolasticTM, SukorezTM or ArkonTM.

5
6 Most preferably the one or more low molecular weight
7 hydrocarbon resins are selected from a group consisting
8 of; Norsolene W90TM, Norsolene W100TM, Norsolene W110TM,
9 Kristalex F85TM, Kristalex F100TM, Kristalex F115TM,
10 Plastolyn 240TM, Plastolyn 290TM, Endex 155TM,
11 Piccolastic D125TM, Sukorez 100TM, Sukorez 120TM, Arkon
12 P100TM, Arkon P125TM, Arkon P140TM, Piccotex 75TM,
13 Piccotex 100TM or Piccotex 120TM.

14
15 Preferably the low molecular weight resin will have a Mn
16 (number average molecular weight) such that it has less
17 than 500 repeating units, and preferably less than 50
18 repeating units.

19
20 The method may comprise the optional step of adding an
21 additive selected from the group consisting of UV
22 inhibitors, antioxidants, flow modifiers, fire retarding
23 agents, colour pigments and brighteners as known in the
24 art.

25
26 Preferably as the polystyrene is mixed with the one or
27 more low molecular weight hydrocarbon resins, the glass
28 transition temperature (T_g) of the material is elevated.
29 Typically the T_g is elevated to 5-10 degrees C higher
30 than the base polymer.

31
32 According to a sixth aspect of the present invention,
33 there is provided a container manufactured from a
34 material that shatters when broken into fragments which

1 do not cut, puncture or otherwise damage human skin or
2 tissue.

3

4 The container may be a bottle, glass, tumbler, or the
5 like.

6

7 Preferably the material is comprised of an amorphous
8 thermoplastic polymer and one or more low molecular
9 weight resins.

10

11 Preferably the amorphous thermoplastic polymer is chosen
12 from the group consisting of: polystyrene (PS), styrene-
13 acrylonitrile co-polymer (SAN), linear polyesters and co-
14 polyesters polycarbonate (PC).

15

16 Preferably the one or more low molecular weight resins
17 are hydrocarbon resins.

18

19 Preferably the one or more low molecular weight resins
20 are aromatic hydrocarbon resins

21

22 The one or more low molecular weight resins chosen will
23 be completely compatible with the chosen polymer. For
24 example, in the case of polystyrene, the low molecular
25 weight resin will typically be C9 aromatic hydrocarbon
26 resin.

27

28 Preferably the material has a tensile stress limit
29 between 11 and 60 Nmm⁻².

30

31 Preferably the one or more low molecular weight
32 hydrocarbon resins are selected from a group consisting
33 of: Norsolene™, Krystalex™, Plastolyn™, Endex™,
34 Piccotex™, Piccolastic™, Sukorez™, Arkon™

1
2 Most preferably the one or more low molecular weight
3 hydrocarbon resins are selected from a group consisting
4 of; Norsolene W90TM, Norsolene W100TM, Norsolene W110TM,
5 Kristalex F85TM, Kristalex F100TM, Kristalex F115TM,
6 Plastolyn 240TM, Plastolyn 290TM, Endex 155TM,
7 Piccolastic D125TM, Sukorez 100TM, Sukorez 120TM, Arkon
8 P100TM, Arkon P125TM, Arkon P140TM, Piccotex 75TM,
9 Piccotex 100TM or Piccotex 120TM.

10

11 Preferably the low molecular weight resin will have a
12 \overline{M}_n (number average molecular weight) such that it has
13 less than 500 repeating units, and preferably less than
14 50 repeating units.

15

16 The container may be manufactured from the material using
17 injection blow moulding and/or injection stretch blow
18 moulding techniques.

19

20 Alternatively, the container may be manufactured from the
21 material using extrusion blow moulding.

22

23 Optionally the material of the container may also
24 comprise a oxygen barrier. The material of the container
25 may also comprise oxygen scavengers.

26

27 The barrier included in the material of the container may
28 be selected from the group consisting of: acrylonitrile-
29 methyl acrylate copolymer, ethylene vinyl alcohol (EVOH)
30 or nylon MXD6.

31

32 Preferably the barrier is BarexTM. Most preferably the
33 barrier is BarexTM 210 or BarexTM 218.

34

1 In the embodiment where nylon MXD6 is used as a barrier,
2 the oxygen scavenger may be X-312. Amosorb 3000, or a
3 scavenger of MXD6 with metal catalysed oxygen reduction
4 chemistry may also be used.
5
6 The barrier may be overmoulded or sprayed onto the
7 container or alternatively may be included in the
8 material of the container, using co-injection techniques.
9
10 The container may also have an inorganic coating. This
11 may be a thin layer of amorphous carbon. The inorganic
12 coating may be applied to the inside surface of the
13 container. Typically the inorganic coating will be
14 applied in a layer of 100 to 200nm thickness. The layer
15 may be applied by spraying.
16
17 The container may also have an external organic coating.
18 The external organic coating may be PVDC or a two
19 component epoxyamine.
20
21 The container may be manufactured from multiple layers of
22 the material. Two or more layers of the container may be
23 combined to act as an improved oxygen barrier.
24
25 Optionally the material of the container may also include
26 UV inhibitors, antioxidants, flow modifiers, colour
27 pigments and brighteners as known in the art.
28
29 Preferably as the amorphous thermoplastic polymer is
30 mixed with the one or more low molecular weight
31 hydrocarbons, the glass transition temperature is
32 elevated. Preferably the material of the container has a
33 glass transition temperature of above 80°C.
34

1 The material herein described can be used as a substitute
 2 for ordinary glass. The material is glass-like in
 3 character having clarity, brittleness, low strain to
 4 failure and rigidity. The material has a variety of uses
 5 including application as enclosures and boxes to house
 6 emergency equipment e.g. keys, first aid boxes, fire
 7 extinguisher, window hammers, emergency stop buttons,
 8 emergency kick out panels and alarms, as well as use in
 9 access panels, windows and doors. It should be
 10 recognised that the abovedescribed uses are by way of
 11 example only and are not intended to limit the manner in
 12 which the material is used. The material can be
 13 manufactured in sheet form, by extrusion, and moulded
 14 into any shape by injection moulding or other standard
 15 melt processes.

16

17 Table 1 shows the stress-strain behaviour of the material
 18 in comparison to other polystyrene materials. Figure 1
 19 shows this information in the form of a graph.

20

Table : Comparison of Properties of Safeglass™ to Polystyrenes.						
Polymer Type:	Modulus / GPa	Yield stress / MPa	Yield strain / %	Stress at break / MPa	Strain at break / %	Vicat softening temperature
Polystyrene (i.e. "crystal" or GPPS)	3.0 - 3.2	Brittle - no yield		4 - 75	2	82 - 98
Toughened polystyrene (e.g. HIPS)	1.6 - 2.4	18 - 38	1.5	< yield	15 - >50	76 - 95
Safeglass™	3.1 - 3.4	Brittle - no yield		8 - 40	1 - 2	95 - 104

21

22 N.B. Safeglass™ materials are slightly more rigid and
 23 certainly more brittle than conventional
 24 "crystal" polystyrene. Modified polystyrenes are
 25 invariably less rigid and tougher materials as a result
 26 of blending with a rubbery (low T_g) additive. This also
 27 results in a lowering of the Glass Transition Temperature

1 (T_g) as witnessed by the reduction in the Vicat Softening
2 Temperature. The reverse is true of Safeglass™ materials
3 which show no such decrease in T_g, indeed it can be
4 higher than the critical temperature.

5

6 The material is fundamentally a blend of a rigid and
7 normally brittle amorphous thermoplastic with a glass
8 transition temperature T_g at least 5° C above ambient and
9 one or more compatible low molecular weight resins.

10

11 An example embodiment will now be described by way of
12 example only.

13

14 A rigid and normally brittle amorphous thermoplastic
15 polymer is blended with one or more low molecular weight
16 resins which have a Mn (number average molecular weight)
17 such that the resin has less than 500 repeating units,
18 preferably less than 50 repeating units. The one or more
19 low molecular weight resins have a weight average
20 molecular weight of 6050 or below.

21

22 The material is manufactured by mixing or blending a
23 clear polymer with one or more low molecular weight
24 hydrocarbon resins. The polymer is an amorphous
25 thermoplastic and can be chosen from the group of
26 polystyrene, (PS), polymethyl methacrylate (PMAA),
27 styrene-acrylonitrile copolymer (SAN), linear polyesters
28 and co-polyesters and polycarbonate (PC). It is important
29 that the low molecular weight resin is completely
30 compatible with the chosen polymer. For example in the
31 case of polystyrene it is C9 aromatic hydrocarbon resin.

32

33 In the herein described embodiment polystyrene is used.

34

1 The one or more low molecular weight resins which are
2 mixed with the polystyrene are aromatic hydrocarbon
3 resins and typically C9 aromatic hydrocarbon resins.
4 The one or more resins are typically alpha methyl styrene
5 or vinyl toluene or derivatives thereof. These are
6 selected from the following group: Norsolene W90TM,
7 Norsolene W100TM, Norsolene W110TM, Kristalex F85TM,
8 Kristalex F100TM, Kristalex F115TM, Plastolyn 240TM,
9 Plastolyn 290TM, Endex 155TM, Piccolastic D125TM, Sukorez
10 100TM, Sukorez 120TM, Arkon P100TM, Arkon P125TM, Arkon
11 P140TM, Piccotex 75TM, Piccotex 100TM or Piccotex 120TM.

12
13 It has been discovered that by blending polystyrene with
14 one or more of the abovementioned low molecular weight
15 hydrocarbon resins, a hard, rigid material is formed
16 which has the appearance and feel of glass, but which is
17 extremely brittle and has low strain to failure. The
18 material also has the inherent advantage that when
19 broken, unlike glass, the material breaks into fragments
20 which are not sharp and do not injure skin or tissue. The
21 material is, by design, manufactured to break between 11
22 and 60 Nmm⁻². Therefore the material, when provided as a
23 substitute to glass, for example in retaining boxes for
24 emergency devices and alarms, can easily be broken by a
25 human hand, fist, elbow, foot or the like and
26 advantageously shatters into fragments or pieces which
27 are not sharp and are not capable of cutting or
28 puncturing human skin. Due to the inherent advantages of
29 the material it is envisaged that it may have a variety
30 of other uses, for example it may have application in
31 novelty toys, such as stress relief toys, or have uses in
32 "stunt" apparatus in, for example, theatres, shows or on
33 film sets.

34

1 The material is manufactured by conventional melt
2 compounding techniques. As the polystyrene is mixed with
3 the one or more low molecular weight hydrocarbon resins,
4 the glass transition temperature (T_g) of the material is
5 elevated as the low molecular weight resin does not have
6 a plasticising effect, the opposite effect is seen as the
7 glass transition temperature of the material is elevated.

8
9 The material is generally transparent or clear, however
10 dyes may be added to change the appearance of the
11 material.

12
13 Low molecular weight in resins is a function of the
14 length of the chains in the resin. In this case the
15 hydrocarbon resins have a very low molecular weight, too
16 low in fact for the resins to be of any use on their own,
17 and are difficult to mould. By mixing low molecular
18 weight hydrocarbon resin with polystyrene, the stress
19 limit of the polystyrene is reduced giving the material
20 the characteristics described in the present Application.
21 Preferably the low molecular weight resin will have a M_n
22 (number average molecular weight) such that it has less
23 than 500 repeating units, and preferably less than 50
24 repeating units.

25
26 The following is an example of the material of the
27 present invention.

28

29 **Example 1**

30 In order to achieve a material with a stress limit of 24
31 Mpa, a 50% mix of polymer and 50% resin is used, which
32 achieves this stress limit. Typically the polymer could
33 be crystal polystyrene such as Polystyrol™ 143E, and
34 resin Plastolyn™ 240.

1

2 **Example 2**

3 In order to achieve a material with a stress limit of 34
4 Mpa, a 60% mix of polymer and 40% resin is used, which
5 achieves this stress limit. Typically the polymer could
6 be crystal polystyrene such as Polystyrol™ 143E, and
7 resin Plastolyn™ 240.

8

9 A container having improved safety characteristics can be
10 manufactured from the material comprised of an amorphous
11 thermoplastic polymer and one or more resins. The resins
12 are aromatic hydrocarbon resins and are selected from a
13 group consisting of Norsolene™, Krystalex™, Plastolyn
14™, Endex™, Sokorez™, Arkon™, Piccolastic™ and
15 Piccotex™, and in particular Norsolene W90™, Norsolene
16 W100™, Norsolene W110™, Kristalex F85™, Kristalex F100
17™, Kristalex F115™, Plastolyn 240™, Plastolyn 290™,
18 Endex 155™, Piccolastic D125™, Sukorez 100™, Sukorez
19 120™, Arkon P100™, Arkon P125™, Arkon P140™, Piccotex
20 75™, Piccotex 100™ or Piccotex 120™. In a particular
21 embodiment the one or more low molecular weight resins
22 are C9 hydrocarbon resins with an \overline{M}_n (number average
23 molecular weight) such that it has less than 500
24 repeating units and preferably less than 50 repeating
25 units. The resin or resins chosen will be selected on
26 compatibility with the chosen polymer.

27

28 Low molecular weight in resins is a function of the
29 length of the chains in the resin. In this case the
30 hydrocarbon resins have a very low molecular weight, too
31 low in fact for the resins to be of any use as a
32 structural plastics material on their own, and are
33 difficult to mould. By mixing low molecular weight
34 hydrocarbon resin with polystyrene, the stress limit of

1 the polystyrene is reduced giving the material the
2 characteristics described in the present Application.

3
4 The amorphous thermoplastic polymer is chosen from the
5 group consisting of polystyrene (PS, styrene-
6 acrylonitrile co-polymer (SAN), linear polyesters and co-
7 polyesters and polycarbonate (PC). These can be mixed,
8 blended or polymerised with the one or more low molecular
9 weight resins. UV inhibitors, dyes, antioxidants, flow
10 modifiers, colour pigments and brighteners can also be
11 added to change or adapt the appearance of the container.

12
13 The container herein described has many characteristics
14 similar to an ordinary glass bottle - i.e. clarity,
15 rigidity and brittleness. However when broken, the
16 bottle shatters into fragments which are harmless and
17 cannot be used to cut or pierce human skin.

18
19 The material used to manufacture the container is
20 fundamentally a blend of a rigid and normally brittle
21 amorphous thermoplastic with a glass transition
22 temperature T_g at least 50°C above ambient and one or
23 more compatible low molecular weight resins. A rigid and
24 normally brittle amorphous thermoplastic polymer is
25 blended with one or more low molecular weight resins
26 which have a \overline{M}_n (number average molecular weight) such
27 that the resin has less than 500 repeating units,
28 preferably less than 50 repeating units. The one or more
29 low molecular weight resins have a weight average
30 molecular weight of 6050 or below. The material is, by
31 design, manufactured to break between 11 and 60 Nmm^{-2} .

32
33 The material can be heated and made into the desired
34 shape of the container, i.e. a bottle, glass or tumbler,

1 by any suitable technique known to the art e.g. injection
2 moulding, extrusion blow moulding or pre-form injection
3 blow moulding techniques.

4
5 The container may be manufactured from one or more layers
6 of the material. More than one layer may be used to
7 provide improved oxygen barrier characteristics.
8 Alternatively the container may be coated with an oxygen
9 barrier. Conventional coating technologies can be broadly
10 divided into two categories. The first are those that
11 use vacuum or plasma routes to deposit very thin films of
12 materials, such as carbon or silica, onto the surface of
13 the article being coated. The second, rely on the
14 atomised spraying of liquid organic materials onto the
15 external surfaces of the bottle. Ideally all coating
16 materials must not interfere with the economics of
17 recycling, nor detract from the bottle's appearance, but
18 a significant further consideration with thin film
19 internal deposits is the need for the materials to be
20 approved for food contact.

21
22 As the container described herein is manufactured from
23 the material at lower processing materials than
24 conventional plastics, barriers which are not usually
25 suitable for this purpose can be used. For example the
26 container can be coated in Barex™ (acrylonitrile-methyl
27 acrylate copolymer), and in particular Barex™ 210 or
28 Barex™ 218, which has high oxygen barrier properties.
29 This can be achieved either by overmoulding, spraying or
30 co-injection techniques. The barrier could alternatively
31 be acrylonitrile-methyl acrylate copolymer, ethylene
32 vinyl alcohol (EVOH) or nylon MXD6. The barrier could be
33 provided on the inside or outside of the container.

34

1 Oxygen scavengers such as all polyester Amosorb 3000 or
2 X-312 scavenger may be used. These Oxygen scavenging
3 materials can be incorporated into the material of the
4 container to react with the gas before it reaches the
5 contents. Amosorb 3000 or X-312 scavenger have particular
6 application when the barrier selected is MXD6 nylon. With
7 these types of active oxygen scavenging packages, shelf
8 life performance is determined solely by the rate of
9 carbonation loss and CO₂ loss is reduced by the presence
10 of the MXD6 as a physical barrier. A scavenger of MXD6
11 with metal catalysed oxygen reduction chemistry may also
12 be used (Oxbar). This system reacts very quickly with
13 oxygen in the container and has a high oxygen capacity,
14 ensuring a long active life.

15
16 The container may also have an inorganic coating such as
17 amorphous carbon. This can be sprayed onto the surface
18 of the container being coated. The inorganic coating can
19 be applied either to the inside or outside of the bottle
20 after blowing. Plasma-applied coatings, using carbon or
21 silicon, which have recently been developed, may be used.
22 The Sidel Actis™ and Kirin DLC™ coating technologies can
23 be used produce a thin layer of amorphous carbon,
24 typically 100 to 200nm thick, on the inside surface of
25 the container. This is deposited from a high-energy
26 plasma of acetylene gas within a high vacuum environment.
27 The coating provides an excellent barrier to both O₂ and
28 CO₂, and, because it is on the inside of the container,
29 prevents the O₂ dissolved in the material of the container
30 from migrating into the contents of the container during
31 the first few weeks of storage.

32
33 Because the deposited layers are fundamentally brittle,
34 they have to be extremely thin in order not to flake off

1 under container stresses, caused by bottle expansion and
2 creep when the bottle is filled, and under pressure from
3 the contents. Other factors include damage and scuffing
4 due to bottle handling, but these clearly do not affect
5 the integrity of the coating if it is on the inside. The
6 barrier performance improvements of carbon coatings are
7 similar to those achieved by organic coatings, again
8 giving a longer potential retail shelf life of around
9 nine months.

10

11 Silica technologies such as Glaskin and BestPet can also
12 be used. These rely on the application of a SiO_x vacuum
13 plasma coating, to give a barrier layer between 40 and
14 60nm thick. While the Glaskin process applies the glass
15 clear coating to the inside of the bottle, the BestPet
16 technique applies it to the outside.

17

18 As an alternative an organic coating may be used.
19 External organic coatings have been known and used in the
20 industry since the early 1980s. In the mid 1990s, barrier
21 coating solutions based on two component epoxyamine
22 chemistry (Bairocade) were developed, first to lengthen
23 the shelf life of the smaller soft drink sizes in hotter
24 climates, and then for beer. These provide a
25 transparent, glossy, external spray coating which is an
26 excellent barrier to migration of CO_2 and O_2 , and is
27 unaffected by humidity. The low temperature thermoset
28 cure provides a tough film, robust to filling and
29 handling conditions.

30

31 Typically the coating will be applied to the container at
32 thicknesses between $6\mu\text{m}$ and $10\mu\text{m}$, and allow the use of
33 standard resins and preforms with existing injection and
34 blow moulding equipment. The use of such coatings

1 provides a performance improvement which is around 19
2 times better than an uncoated container and translates
3 into a longer retail shelf life. The external organic
4 coating may be PVDC two component epoxyamine.

5
6 The alternative approach to improving the gas permeation
7 properties of the container material is to manufacture it
8 from multiple layers of the material. In other words,
9 two or more layers of the container may be combined to
10 act as an improved oxygen barrier. Final shape blowing
11 produces a bottle with up to seven different polymer
12 layers, which either act as a physical barrier to gas
13 permeation, or are chemically active in scavenging oxygen
14 from the material of the container and intercepting
15 oxygen diffusing in from outside.

16
17 The material herein described has an elevated glass
18 transition temperature, which is much higher than the
19 glass transition temperature of, for example, PET. PET
20 has a glass transition temperature that is lower than the
21 pasteurisation temperature used in the beer industry. As
22 a result when PET is used in the manufacture of bottles,
23 creep may occur during filling. In other words the
24 material expands, which causes deformity of the bottle.
25 This problem is eliminated using the material herein
26 described as the glass transition temperature is above
27 the pasteurisation temperature used during filling.

28
29 Furthermore, bottles made from PET are generally filled
30 using flash pasteurisation, as opposed to full
31 pasteurisation, which the industry prefers. Full
32 pasteurisation is generally more efficient which results
33 in a longer shelf life for the product. However full
34 pasteurisation is not generally used with PET materials.

1 A particular advantage of the material herein described
2 is that because it has an elevated glass transition
3 temperature, it can withstand full pasteurisation.
4

5 It has been discovered that using the above described
6 material a container such as a bottle, glass or tumbler
7 can be manufactured which does not cut, puncture or
8 otherwise damage human skin or tissue when broken. In
9 other words, the container will shatter into harmless
10 fragments, shards or pieces when broken.
11

12 A particular advantage of the container described herein,
13 lies in the fact that even though it does not shatter
14 into dangerous fragment when broken, it has a similar
15 quality feel as glass, and has improved aesthetic
16 qualities over existing plastics such as PET. The
17 material herein described for use in manufacturing a
18 container, is relatively light and glass-like to touch
19 and as it is a polymer is can be processed, for example
20 by including oxygen barriers during production.

21 Importantly, the material is thicker than an equivalent
22 PET bottle so has a more glass-like feel but can be
23 manufactured into containers without an increase in cost.
24

25 Potential uses of the container are not limited. For
26 example, the container may be used for beer, carbonated
27 soft drinks, oxygen sensitive juices, beverages or milk
28

29 Example 1

30

31 An 85% mix of polystyrene polymer and 15% resin is used
32 to manufacture a bottle with improved safety
33 characteristics. The 15% resin maybe comprised of a
34 single resin selected from the group consisting of

1 NorsoleneTM, KrystalexTM, PlastolynTM, EndexTM, Sokorez
2 TM, ArkonTM, PiccolasticTM and PiccotexTM, or may be a
3 combination of two or more of the above. PlastolynTM is
4 particularly suitable for this purpose. The resin or
5 resins are selected to achieve a desired molecular weight
6 range.

7
8 Further modifications and improvements may be added
9 without departing from the scope of the invention herein
10 intended.

11
12
13